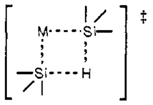
for reactions between d^0 M–R (R = H, alkyl, aryl) and C–H bonds.[8] The mechanism for the photochemical σ-bond metathesis



process is currently under investigation. Photochemical activation of CpCp*M(SiRR′R″)Cl (M = Zr, Hf) derivatives appears to result from excitation of low-intensity transitions in the visible region. In pentane the absorptions for **1** and **4** appear at 461 nm (ϵ = 500) and 405 nm (ϵ = 445), respectively, and are responsible for the observed photochemistry as determined by use of cutoff filters. It seems likely that these transitions involve silyl ligand to metal charge transfer, since they do not appear in UV–vis spectra of analogous alkyls, and there is a significant shift of the transition to higher energy on changing the metal from zirconium to hafnium. With a 365 (±5) nm band pass filter, the quantum yield for the reaction of **4** with $PhSiH_3$ in benzene-d_6 is 0.97. Given this relatively high quantum yield, it is difficult at this time to rule out a radical chain mechanism.

Previous studies have shown that photolysis of alkyl derivatives of the type Cp_2MR_2 (M = Ti, Zr) results in metal–carbon bond homolysis.[9] However, currently we have little chemical evidence for photochemical homolysis of the metal–silicon bonds in **1** and **4**. For example, no radical coupling products have been observed, and photolysis by visible light does not initiate polymerization of styrene or methyl methacrylate. Also, the photochemical reaction of **4** with ^tBuBr, a good silyl radical trapping reagent,[10] is much slower than the corresponding reaction with $PhSiH_3$. The photochemical reaction of **4** with $PhSiD_3$ quantitatively gives $CpCp^*Hf(SiD_2Ph)Cl$ and $DSi(SiMe_3)_3$ (by ^1H and ^2H NMR). Reaction times for the photochemical reaction of **4** with silanes are strongly influenced by steric requirements of the incoming silane. Whereas the concentration of small primary silanes does not influence reaction times, bulkier silanes (e.g., 2,4,6-$Me_3C_6H_2SiH_3$ and secondary silanes) show a strong concentration dependence. Additionally, small Lewis bases (e.g., pyridine and PMe_2Ph) but not large ones (e.g., PCy_3) strongly inhibit these photochemical and thermal σ-bond metathesis reactions. It therefore appears that these processes may require an empty coordination site at the metal. Future studies will characterize further mechanistic details for these reactions.

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Supplementary Material Available: Characterization data (^1H NMR, $^{13}C\{^1H\}$ NMR, ^{29}Si NMR, IR, UV–vis, and elemental analyses) for new compounds (4 pages). Ordering information is given on any current masthead page.

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(8) (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981. (c) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425. (d) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (e) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4064. (f) Watson, P. J.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

(9) (a) Van Leeuwen, P. W. N. M.; Van der Heijden, H.; Roobeek, C. F.; Frijns, J. H. G. *J. Organomet. Chem.* **1981**, *209*, 169. (b) Hudson, A.; Lappert, M. F.; Pichon, R. *J. Chem. Soc., Chem. Commun.* **1983**, 374. (c) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977**, *141*, 299. (d) Samuel, E.; Maillard, P.; Giannotti, C. *J. Organomet. Chem.* **1977**, *142*, 289.

(10) Lehnig, M.; Werner, F.; Neumann, W. P. *J. Organomet. Chem.* **1975**, *97*, 375.

Specific Assemblies of the Naphthalene Unit in Monolayers and the Consequent Control of Energy Transfer[1]

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We describe in this paper controlled organization and the consequently modified fluorescence behavior (emission and sensitization of anthracene fluorescence) of the naphthalene unit in surface monolayers.

The fluorescence behavior of surface monolayers[2-6] is attracting much attention because it can provide fundamental data on the transfer processes of energy and electron. Chromophore orientation plays a decisive role in these processes, as attested by recent determination of the 3D structure of the bacterial photosynthetic reaction center.[7] Naphthalene and anthracene units are a representative chromophore pair in the organic energy-transfer process. Therefore, we chose amphiphiles **1** and **2** in this study. They form bilayer membranes[8,9] and are suitable as monolayer components.

As shown in Figure 1,[10] the naphthalene amphiphile produces a condensed monolayer on pure water with molecular area of 0.50 $nm^2 \cdot molecule^{-1}$ and collapse pressure of 40 $mN \cdot m^{-1}$. A somewhat expanded monolayer is formed (molecular area, 0.58 $nm^2 \cdot molecule^{-1}$) in the presence of dextran sulfate (DEX) in the subphase. Carboxymethylcellulose (CMC) in the subphase produces a much more expanded monolayer (molecular area, ca. 0.80 $nm^2 \cdot molecule^{-1}$). Similar polyanion effects have been found for monolayers of azobenzene-derived, single-chain ammonium amphiphiles.[12,13] These specific π-A changes are produced by polyion complex formation at the air–water interface, and this technique would have a general usefulness for controlling the molecular packing in charged monolayers.

Monolayer **1** gives a structured fluorescence spectrum (Figure 2a) which was characteristic of the crystalline aqueous bilayer membrane.[8] This spectral pattern does not change with the progress of compression, and the intensity fluctuation is observed in the low pressure region (ca. 2 $mN \cdot m^{-1}$). These data indicate that the crystalline monolayer island is formed on water even without compression.

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(1) Contribution No. 895 from the Department of Organic Synthesis.

(2) Tweet, A. G.; Gaines, G. L., Jr.; Bellamy, W. D. *J. Chem. Phys.* **1964**, *40*, 2596–2600.

(3) Aoshima, R.; Iriyama, K.; Asai, H. *Appl. Optics.* **1973**, *12*, 2748–2750.

(4) Grieser, F.; Thistlethwaite, P.; Triandos, P. *J. Am. Chem. Soc.* **1986**, *108*, 3844–3846.

(5) Florsheimer, M.; Mohwald, H. *Thin Solid Films* **1988**, *159*, 115–123.

(6) Gonen, O.; Levanon, H.; Patterson, L. K. *Isr. J. Chem.* **1981**, *21*, 271–276.

(7) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *Nature (London)* **1985**, *318*, 618–624.

(8) Nakashima, N.; Kimizuka, N.; Kunitake, T. *Chem. Lett.* **1985**, 1817–1820.

(9) Shimomura, M.; Hashimoto, H.; Kunitake, T. *Chem. Lett.* **1982**, 1285–1288.

(10) The surface pressure area isotherms (π-A curve) were obtained with a computer-controlled film balance (San-esu Keisoku, Japan, Model FSD-20)[11] at a compression rate of 6 × 10^{13} $nm^2 \cdot s^{-1}$ at 20 °C on pure water (Milli-Q II system, Millipore Co.). Amphiphiles were dissolved (10 mg/10 mL) in a 7:1:2 mixture of benzene, CH_2Cl_2, and ethanol and spread on water evenly. Fluorescence spectra of surface monolayers were measured with an intensified multichannel photodetector system (Otsuka Electronics, Japan, Model IMUC 7000). A Xenon lamp with a band pass filter (λ_{max} 278 nm, half band width 14 nm) was used as light source. The incident light through an optical fiber was directed at an angle of 45° against water surface, and emission was detected by a vertically positioned optical fiber. The sampling time of a whole spectrum was 5 or 10 s.

(11) Shimomura, M.; Kunitake, T.; Inoue, H.; Ono, N. *Nippon Kagaku Kaishi* **1987**, 2058–2063.

(12) Shimomura, K.; Kunitake, T. *Thin Solid Films* **1985**, *132*, 243–248.

(13) Kimizuka, N.; Kunitake, T. *Chem. Lett.* **1988**, 827–830.

0002-7863/89/1511-3758$01.50/0

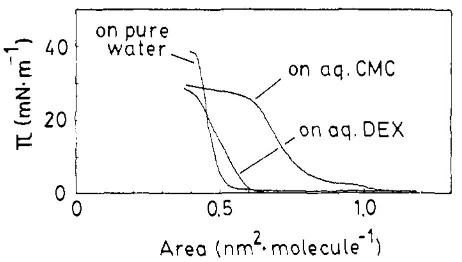
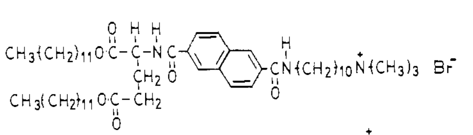
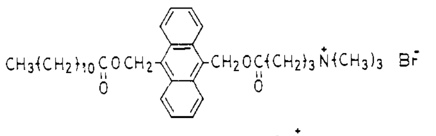


Figure 1. π-A curves of **1** at 20 °C. Polyanion, 1.0 × 10^{-4} unit M.

Chart I



1 $2C_{12}$-L-Glu-Naph-$C_{10}N^+$



2 C_{12}-Anth-C_4N^+

A polyion-complexed monolayer with DEX gives the analogous fluorescence behavior, though with enhanced intensity (1.5–2 times). In contrast, a new emission peak is found on aqueous CMC at 365 nm with vibrational structures at longer wavelengths. This is located in between the monomer-like peak (λ_{max} 354 nm) and the broad excimer peak (λ_{max} 414 nm) of the corresponding aqueous bilayer.[8] Somewhat similar emissions were found for poly(vinylnaphthalenes) and attributed to dimers[14] and second excimers.[15,16] Thus, aqueous CMC produces an expanded monolayer with different naphthalene packing which gives rise to an altered fluorescence pattern.[17]

Energy transfer in monolayers should be controlled by alteration of the chromophore packing. Figure 2b shows fluorescence spectra of naphthalene monolayer **1** containing 1 mol % of anthracene component **2**.[18] On aqueous dextran sulfate, emissions typical of the naphthalene monolayer are observed together with emissions due to the anthracene component at 402 and 424 nm even at low compression. The single-component anthracene monolayer on aqueous polyanions gives broad excimer emissions at 480–490 nm. Therefore, we conclude that the anthracene component in the mixed monolayer exists in the monomeric dispersion and that energy migration among naphthalenes and the subsequent energy transfer to anthracene occur, as illustrated by the insert of Figure 2b. The emission pattern remains the same upon further compression, although the intensity is enhanced.

When the subphase contains CMC, the anthracene emission is not clearly detected. Apparently, the excitation energy is trapped by emission sites of naphthalene (dimers or second excimers) during energy migration and is not efficiently transfered to the anthracene unit.

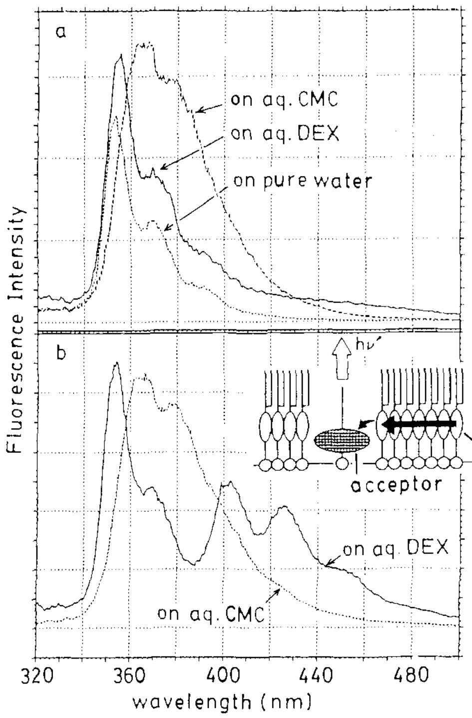


Figure 2. Fluorescence spectra of surface monolayers. Polyanion, 1.0 × 10^{-4} unit M; 20 °C. a, **1** at 1.0 nm^2·molecule^{-1}. The spectral shapes do not change at higher pressures. b, **1**/**2** = 100/1 (mol/mol) at 20 mN·m^{-1}.

In conclusion, we demonstrated directly on water that the altered orientation of the naphthalene monolayer by polyion complexation lead to controlled energy transfer to the anthracene component. Although energy transfer among chromophores in matrix monolayers has been reported,[5,6] the use of self-assembling monolayers with controllable orientation is advantageous as a step toward construction of highly organized, photofunctional molecular systems.

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[14] Irie, M.; Kamijo, T.; Aikawa, M.; Takemura, T.; Hayashi, K.; Baba, H. *J. Phys. Chem.* **1977**, *81*, 1571–1574.

[15] Itagaki, H.; Obukata, N.; Okamoto, A.; Horie, K.; Mita, I. *Chem. Phys. Lett.* **1981**, *78*, 143–146.

[16] Nakahira, T.; Ishizuka, S.; Iwabuchi, S.; Kojima, K. *Macromolecules* **1982**, *15*, 1217–1218.

[17] Blue shifts were observed for the naphthalene ${}^1B_b$ band of the surface monolayer relative to that in ethanol, and large hyperchromic effects were found at 300 and 350 nm for the monolayer on pure water and on aqueous DEX but not on aqueous CMC. Fluorescence microscopy studies of the monolayers of **1** containing 0.5% of octadecyl rhodamine B at low surface pressures indicated the presence of crystalline domains on pure water, of noncrystalline islands on aqueous DEX, and of uniform monolayers on aqueous CMC.

[18] The anthracene derivative **2** did not form a stable monolayer on pure water, and a mixed monolayer of **1** and **2** did not display sensitized fluorescence under the same conditions. Thus, all the energy-transfer experiments were conducted on aqueous polyanions. Addition of the anthracene component did not affect the π-A characteristics of **1**.

On the Metal Ion Specificity of "Zinc Finger" Proteins

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A class of proteins characterized by the presence of one or more sequences of the form Cys-$X_{2,4}$-Cys-X_3-Phe-X_5-Leu-X_2-His-$X_{3,4}$-His (often called "zinc finger" proteins) has been discovered and characterized in recent years.[1-3] Each of these sequences appears to bind a zinc ion in a tetrahedral site formed by the invariant cysteine and histidine residues. The geometry of the site is supported by EXAFS studies[4] and by spectrophotometric studies of Co^{2+}-substituted "zinc finger" peptides[5,6] and of appropriate synthetic model complexes.[7,8] Studies of several of these

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[1] Klug, A.; Rhodes, D. *Trends Biochem. Sci.* **1987**, *12*, 464.

[2] Evans, R. M.; Hollenberg, S. M. *Cell* **1988**, *52*, 1.

[3] Berg, J. M. *Met. Ions. Biol. Sys.* **1989**, *25*, 235.

[4] Diakun, G. P.; Fairall, L.; Klug, A. *Nature* **1986**, *324*, 698.

[5] Frankel, A. D.; Berg, J. M.; Pabo, C. O. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 4841.

[6] Pārraga, G.; Horvath, S. J.; Eisen, A.; Taylor, W. E.; Hood, L.; Young, E. T.; Klevit, R. E. *Science* **1988**, *241*, 1489.

[7] Corwin, D. T., Jr.; Fikar, R.; Koch, S. A. *Inorg. Chem.* **1987**, *26*, 2079.

[8] Corwin, D. T., Jr.; Gruff, E. S.; Koch, S. A. *J. Chem. Soc., Chem. Commun.* **1987**, 966.